WILLIAM MARSH RICE UNIVERSITY

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On

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Covering

Research on the Physics of Solid Materials

For the Period November 1, 1963 to April 30, 1963

Under the Direction of

Franz R. Brotzen

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This grant has been in effect for four years. The objective of the grant can be summarized as follows: The performance of fundamental research on the behavior and properties of solid materials and the simultaneous promotion of graduate education of scientists and engineers in this field. This objective has been pursued at Rice with considerable success as evidenced by the achievements during the six months covered by this report.

At present there are 29 different research projects supported by this grant. These projects are carried out under the direction of 15 faculty members in 5 different departments of the University, i.e., the Departments of Chemical Engineering, Chemistry, Electrical Engineering, Mechanical Engineering and Physics. A new project dealing with the fundamental aspects of fracture in crystals performed by members of the Department of Geology is being added to this list. During the last six months, in addition to seven post-doctoral fellows, 29 graduate students worked on projects sponsored by this grant. In the period covered by this report, six papers were published and ten manuscripts were submitted to journals for publication resulting from work carried out under the grant. These are summarized in an appendix to this report.

I. Solid State Physics

(a) Spin-Lattice Interactions in Paramagnetic Crystals

Dr. P. L. Donoho, Department of Physics

Work is continuing on effects of uniaxial stress in ruby and calcium fluoride and on ultrasonic spin-resonance absorption in the same materials. Some of this work has been reported at the American Physical Society meeting in Houston on February 28 - March 2, 1963.

(i) Attenuation of 9.3-Gc Elastic Waves in U-Doped CaF_2.
The attenuation of 9.3 Gc [111] longitudinal elastic waves in CaF_2 containing U ions has been observed as a function of the magnitude and direction of an external dc magnetic field. The sample utilized was a cylindrical rod 0.3 cm in diam and 1.83 cm long, with axis along the [111] direction, ostensibly doped with 0.1% U^{3+} ions. However, the observed absorption at approximately 1.6°K indicated the presence of other ions. A subsequent ERP analysis revealed that the crystal also contains U^{4+} ions in a significant amount. The observed attenuation has thus been attributed to the spin-lattice interaction between the U^{4+} ions and the host CaF_2 lattice. The experimental method was that previously employed in this laboratory.

(ii) Spin-Lattice Relaxation Times for Iron-Group Ions.
Recent measurements on acoustic spin resonance and on the effect of uniaxial stress on ESR spectra have yielded important information on spin-phonon couplings for Fe-group ions in insulating crystal lattices. The results of such experiments have been interpreted in terms of an effective spin-lattice Hamiltonian, quadratic in spin operators and linear in lattice strain operators. Because it is linear in strain, this spin-lattice Hamiltonian can be used to compute 1-phonon spin-lattice relaxation times. Rough estimates have been made for spin-lattice relaxation times using the spin-lattice Hamiltonian but neglecting crystalline anistropy; order-of-magnitude agreement with measured relaxation times is obtained using such estimates. Since a more careful comparison of calculated and experimental relaxation times is desirable, we have computed 1-phonon spin-lattice relaxation times accurately taking anistropy into account.

(iii) Splitting of Paramagnetic-Resonance Lines of Cr^{3+} in Ruby by Applied Stress
Splitting of the paramagnetic resonance lines of Cr^{3+} in ruby has been induced by the application of uniaxial compressive stress along a direction not parallel to the c axis. This strain-dependent splitting is attributed to the fact that the Cr^{3+} ion enters the Al_2O_3 lattice substitutionally in 2 nonequivalent sites, and, therefore, an applied stress may distort the crystalline field differently for these sites. The angular dependence of the splitting has been observed at room temperature at a frequency of 10.1 Gc for strains up to $4X10^{-4}$, and the results may be described by an additional term in the spin Hamiltonian of the form $D_{ij}S_iS_j$, where D_{ij} is a symmetric, traceless tensor that can be written in terms of the strain components e_{kl} as $D_{ij} = G_{ijkl}e_{kl}$.

(b) Studies of Nuclear Spin-Lattice Relaxation Times in Paramagnetic Crystals
Dr. Ben Josephson, Jr., Department of Physics

The nuclear spin-lattice relaxation time, T_1, for F^{19} nuclei in single crystals of calcium fluoride (CaF_2) doped with uranium and Europium has been measured as a function of temperature from 1.3°K to 300°K. Measurements of T_1 as a function of temperature in samarium-doped CaF_2 for the same temperature range are presently being made and will be completed soon.

(i) $CaF_2:E_u$ (0.13 by weight): T_1 is virtually temperature-independent from 1.3°K to 50°K. Above 50°K, T_1 decreases rapidly with increasing temperature. The temperature dependence becomes as strong as $T^{-2.3}$ (approximate) around 100°K, but becomes somewhat weaker as room temperature is approached. Qualitative agreement with theoretical predictions is obtained if the correlation time of the impurity spin is determined by temperature-independent spin-spin interaction at temperatures below 50°K. The temperature-dependent impurity spin-lattice interaction becomes stronger as the temperature is increased, and becomes dominant above 50°K, where T_1 becomes strongly temperature dependent.

(ii) CaF_2: U (0.1% by weight): The variation of T_1 with temperature for this crystal appears completely different from that observed for $CaF_2:E_u$ because a much stronger impurity spin-lattice interaction. Four separate regions can be identified. Approximately:

$T < 15^\circ K$:	$T_1 \cong T^{-1.3}$
$15^\circ K < T < 25^\circ K$:	$T_1 \cong T^{-7}$
$30^\circ K < T < 80^\circ K$:	$T_1 \cong T^{2.5}$
$100^\circ K < T < 300^\circ K$:	$T_1 \cong T^{0}$

Qualitative agreement with the theory can be obtained for the first three regions. The fourth region suggests that the impurity-spin correlation time is no longer determined by spin-lattice interaction above 100°K. Other possibilities (e.g., lattice diffusion) are being considered.

In the next six months, we will complete taking date on $CaF_2:Sm$, and we also propose to investigate $CaF_2:Nd$ if we can obtain a sample. A detailed analysis of the data in the light of theoretical predictions will also be made.

(c) Phonon-Magnon Interactions in Thin Ferromagnetic Films
Dr. P. L. Donoho, Department of Physics

Phonon generation by spin-wave (magnon) interactions has been studied by M. P. Maley and P. L. Donoho with preliminary very interesting results being obtained which indicate that understanding of the spin-lattice interaction in ferromagnets is poor at present. This approach to the problem will yield very useful information not obtainable by other means on properties of magnetic thin-films, such as used in computers.

(d) Phonon-Phonon Interactions
Dr. B. Josephson, Jr., Department of Physics

A study of this process has been undertaken but no results have as yet been obtained because of instrumentation problems. (Applications to thermal conductivity studies in solids.)

(e) Laser Research
Dr. T. A. Rabson, Department of Electrical Engineering

The effects of magnetic fields of up to 8000 gauss on the light output of ruby lasers have been investigated for various temperatures, pumping powers, and ruby crystals. The polarization, power output and, multimode mixing of the light output have been measured as a function of magnetic field. An article on the work is being prepared for submission to the Proceedings of the IEEE for publication.

Work on magnetic field effects on ruby laser output will be extended to the case where Q spoiling techniques are employed. Also, nonlinear effects in KDP crystals as a result of incident high power laser beams, such as harmonic production, will be studied.

(f) Superconductivity of Niobium
Dr. W. V. Houston, Department of Physics

The past six months have been devoted to the effort to find out whether a moderately large wire of fairly pure niobium will continue in the superconducting state when carrying a current large enough to produce at the surface of the wire the generally accepted critical field for niobium. In other words, this is a test of Silsbee's hypothesis as applied to a niobium wire. It is proposed to do this for both direct and alternating currents, but since preliminary work raised some doubts, it seemed worthwhile to establish the fact for direct current first.

The difficulties have been those of instrumentation. Two problems have been met and are now apparently solved. The first refers to the making of a suitable contact between a niobium wire and some other conductor such as copper. This contact must withstand the differential contraction as the system is cooled and must of course maintain low resistance. The present solution is to wrap a piece of niobium wire with a thin sheet of indium and to press it against copper or brass in mechanical tension. Because the copper or brass contracts faster than the niobium, this tension is maintained at low temperatures and apparently the interposition of indium provides a good contact which did not seem to exist when it was omitted.

The second problem has been the design of a suitable means of leading the heavy current into a low temperature region without undue heat loss. The present solution is to provide a lead-in conductor of a large number of separate strands arranged in such a form as to give maximum surface to cooling by the helium vapors which are constrained to rise through it. Apparently in this way the heat capacity of the helium gas rising from the liquid can be utilized rather effectively in keeping the leads at a low temperature so that the resistance loss is minimized.

With these two elements incorporated into an apparatus, it is hoped within a short time to get more accurate measurements than has thus far been possible on the limiting current in a superconducting niobium wire some two millimeters in diameter.

II. Physical Metallurgy

(a) The Temperature Dependence of the Microyield Points in Prestrained Magnesium Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

The experimental results of this project were reported in Semiannual Status Report #7 and a manuscript has been forwarded to NASA. This manuscript should be considered as in rough form, since the authors feel extensive revision is necessary prior to publication. The material in this paper was presented at the 92nd Annual Meeting of the AIME in Dallas, Texas, February, 1963.

(b) The Effect of Controlled Solute Atom Addition and Temperature (below 82°K) Upon the Damping Loops in Magnesium Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

The aims and general purpose of this project were outlined in the last three semiannual status reports. To date, 35 single crystals of magnesium and magnesium alloys have been grown from the melt. 19 of these have suitable orientations for testing in tension (i.e., $30^\circ \leq \theta \leq 60^\circ$, where θ is the angle between the normal to the basal plane and the specimen axis). The alloyed crystals contain 0.01, 0.02, 0.05, 0.10 and 0.50 atomic % Al, 0.10 atomic % Zn, 0.10 atomic % Cd, 0.10 atomic % Th and 0.10 atomic % In, respectively. Twenty-seven crystals have been sectioned and gripped. Preliminary data has been obtained at room temperature on one of the Mg-Zn crystals, as regards the change in modulus and decrement with prestrain. The helium cryostat built for microstrain measurements between 10 and 425°K is almost completed. It has considerable flexibility with respect to dismantling.

(c) Microcreep in Single Crystals of Magnesium
Dr. J. M. Roberts, Department of Mechanical Engineering.

A substantial portion of this investigation is now completed. The main results are:

(i) Reliable microcreep data (strain rates as low as 10^{-9} sec^{-1}) has been obtained over the temperature range 77 to 300°K to an accuracy of $\pm$ 3.2%.

(ii) The time law for microcreep of magnesium crystals over the temperature range 77 to 300° can be characterized by

$$\gamma = \alpha \ln (1 + At) \text{ where}$$

γ is the resolved shear microstrain, t is time and α and A are constants. A does not appear to be temperature dependent but is possibly dependent upon the magnitude of the load increment. The constant α was a function of several parameters but seemed to be best described experimentally as a function of the total strain resulting during an incremental creep test.

(iii) The effective activation volume was found to be independent of applied stress. It was proportional to temperature such that

$v^* = 2.38 \times 10^{-21} T \text{ cm}^3$ for an ultra high purity crystal and

$v^* = 2.28 \times 10^{-21} T \text{ cm}^3$ for an alloyed crystal containing 0.046% Al

Strain rate change tests during measurement of the stress-microstrain curve gave results consistent with the microcreep data.

(iv) Attempts to measure the effective activation energy associated with microcreep were only partially successful. The problem lies in the fact that even maintaining about 80% of the total stress on the specimen, pronounced recovery of the crystal to creep transiently occurs during a temperature change. The effective activation energy appears to be less than 0.5 ev. at an applied stress of 30 gm/mm^2.

(v) The most significant result of this study is the determination of the effective stress acting upon dislocation during microcreep. This was done by measuring the internal stress by balancing the load at the point where forward microcreep ceased, a slightly lower load results in creep recovery. In this way the internal stress has been evaluated to be about 0.93 of the applied stress over the entire preyield stress region. It is intended to measure the effective stress over a range of temperature, in doing so, it is believed a significant value of the effective activation energy can be obtained. This can be done by noting the initial strain rate as a function of temperature for a constant value of the effective stress. Should this procedure prove reliable, an innovation to creep studies will be available.

(d) Dislocation Damping in Copper Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

This work represents completion of a portion of the study previously described as "Effect of Radiation Damage Upon Damping Loops in Copper Single Crystals". Due to unforeseen difficulties in getting the copper crystals irradiated, to date, no results are available for radiation damaged crystals. The following results, however, have been obtained.

(i) The decrement associated with damping loops in 99.999% pure copper single crystals was found to decrease markedly with prestrain. For prestrains greater than 1% only small decrements (less than 0,03) could be observed below stress amplitudes of 250 psi. No temperature dependence of the decrement was noted in the range 135 to 300°K.

(ii) The microyield point, or the stress level at which an open hysteresis loop was first observed, was found to increase with prestrain, but to be independent of temperature between 135 to 300°K. Numerous stress-strain curves indicated that the crystals exhibited only a limited easy glide region ($\gamma_p < 0.2\%$).

(iii) The early onset of State II hardening can best be explained as a specimen size effect. The microyield point appears to be associated with the stress necessary to operate a Frank-Read source. The prestrain dependence of the decrement and of the stress to create an open loop are thought to be, due principally to the shortening of the average dislocation network loop length in the State II region. Interpretation of the results in this manner is ambiguous, however, since an increasing mean internal stress field could also explain the results, at least in part.

It is planned to extend this work to also include irradiation effects as originally planned.

(e) The Temperature Dependence of the Activation Volume, Work-Hardening Coefficient and Flow Stress of Cadmium Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

Over the past six months, considerable effort has been made at understanding the origin of the anomalous activation volume, flow stress and work-hardening characteristics of cadmium.Correlation between the results obtained in this laboratory and the electrical resistivity after cold work studies of Peiffer at Rias as well as comparison with the results of Trauble and Seeger on the plastic deformation of zinc suggest:

(i) Flow between 77 and 150°K is controlled by cutting of the dislocation forest by glide dislocations

(ii) Flow between 150 to 300°K is controlled by the resistence of negative Frank partial dislocations to glide dislocations.

(iii) Flow above 300° is controlled by the climb of almost pure screw dislocations.

Some preliminary creep runs have been made to check out the anomalous behaviors. This work is not complete enough for a final report.

(f) Lattice-Imperfection Study of Body-Centered Cubic Metals
Dr. F. R. Brotzen, Department of Mechanical Engineering

The first portion of the experimental investigation had been concluded prior to the work period covered by this report. In order to prepare a final report for publication, it became necessary to correlate the experimental observations with a possible model. The stress and the strain dependences of the activation volume were determined in zone-refined single crystals of molybdenum, tested in simple shear on the (110) in the [1$\bar{1}$1], Interpretation of the results points at a mechanism of deformation in molybdenum which is based on the non-conservative movement of jogs in the low-temperature range. A sudden rise of the activation volume at temperatures above 300°K can be explained as caused by conservative movement of jogs as

a thermally activated process. It is proposed that the dramatic rise of the flow stress at low temperatures is due to the lack of conservative motion of jogs along screw dislocations. The activation volume becomes quite low because of accumulation of jogs, thereby giving rise to high strain-rate and temperature sensitivities of the stress.

(g) Transient Creep in Molybdenum Single Crystals
Dr. F. R. Brotzen, Department of Mechanical Engineering

Incremental loading tests were performed on molybdenum single crystals in direct shear, oriented for slip on the (110)- Plane and in the [111]-direction at temperatures from 125°K to 300°K. The resulting transient creep could not be described by the logarithmic creep relation $\dot{\epsilon} = A/(1+t)^m$ as it can for the close-packed metals; however, the equation $\dot{\epsilon} = Ae^{-B\Delta\epsilon} + Ce^{-D\Delta\epsilon}$ was found to fit the data well. Activation volumes calculated from the relation $v^* = kT \frac{\ln C - \ln \dot{\epsilon}_i}{\Delta\tau_a}$ agreed very closely with those reported by Youngblood (Thesis, Rice University, 1963).

The region characterized by $Ae^{-B\Delta\epsilon}$ was effective only over very small ranges of $\Delta\epsilon$, with $Ce^{-D\Delta\epsilon}$ subsequently controlling deformation. Difficulty of measurement limited most of the interpretation to $Ce^{-D\Delta\epsilon}$. Analysis is presented which indicates that a Peierls model may be the rate-controlling mechanism for this region.

Studies of orientation dependence were made which indicated that slip in the [111]- direction occurs most easily on the (110)- planes, is slightly more difficult on the (123)- planes, and is substantially more difficult on the (112)- planes.

(h) Microwave Ultrasonic Absorption in Lithium Fluoride Crystals
Drs. P. L. Donoho, Department of Physics, J. M. Roberts and F. R. Brotzen, Department of Mechanical Engineering

Work has been delayed on this problem because of lack of suitable personnel. It will be resumed in the summer of 1963.

All of the projects (a) to (h) are designed at gaining a better understanding of the behavior of dislocation and point defects, so necessary for a general understanding of the mechanical properties of solids.

(i) Electron Microscopy
Dr. W. B. Pfeiffer, Department of Mechanical Engineering

For the accommodation of a new electron microscope, Philips EM 200, five laboratories were planned, built and arranged. The electron microscope has been installed recently.

The first investigation with the EM 200 will be concerned with precipitation in gold alloys and will use the transmission technique.

Theoretical work that has been done may be summarized as follows: Earlier work [phys. stat. sol. 3, (1963)]on the kinematical theory of electron diffraction contrast of dislocations in thin metal foils has been continued by studying the influence of finite specimen dimensions. As a first step the elastic displacement field of a special edge dislocation in half space has been calculated. In cooperation with Dr. R. M. Asimow, a study is planned on the influence of short-range order in alloys on the deformation dependence of the electrical resistivity.

(j) Quenched-in Resistivity
Dr. R. M. Asimow, Department of Mechanical Engineering

Work has been completed on the quenched-in resistivity of dilute Au-In and Au-Ag alloys for low quenching temperatures. Results for high-temperature quenches did not fit the theory. It is thought that this is due to insufficient quenching rate and modifications are being made in the quench furnace and experimental set-up to permit faster quench rates.

(k) Relaxation Times for Coherent Paramagnetic Particles
Dr. R. M. Asimow, Department of Mechanical Engineering

The model being studied consists of spherical single domain ferromagnetic particles imbedded in a non-magnetic matrix. The particles have uniaxial crystalline anistropy, thus an easy direction of magnetization. For many directions of magnetization there are energy barriers to overcome before a particle with its direction of magnetization initially in some arbitrary direction can rotate toward the easy direction of magnetization. In the model, the energy to overcome the barriers is supplied by the coupling between the lattice phonons and the magnetization caused by the magnetostriction effect. The results of the analysis give a relaxation time in terms of certain fundamental material properties.

(l) Partial Molal Free Energies of Interstitial Solid Solutions in F.C.C. Lattices
Dr. R. M. Asimow, Department of Mechanical Engineering

A theoretical analysis is under way which it is hoped will yield partial molal free energies in interstitial solid solutions from a somewhat more fundamental basis than in the past. It is planned to use this same procedure to calculate the change in interstitial diffusivity with concentration.

(m) X-Ray and Resistivity Studies of Ti-V Alloys
Dr. F. R. Brotzen, Department of Mechanical Engineering

At this time, the equipment necessary for the x-ray diffraction studies has been completed and is ready for immediate use. This consists of:

(i) An x-ray cryostat for x-ray diffraction studies at temperatures down to -160°C.

(ii) The associated temperature control assembly for the cryostat.

(iii) A high-vacuum (10^{-5} mm. Hg) vertical tube furnace with an associated temperature control system for heat treatment of the alloys up to 1000°C. It is possible to quench out of this furnace at 1000°C and 10^{-5} mm Hg to 0°C and atmospheric pressure in less than 1 second.

(iv) A digital scaler and print out recorder for obtaining a permanent record of the x-ray diffraction data.

Work on the resistivity measurements is tentative and dependent on the results of the x-ray diffraction studies.

The last four research projects center about basic aspects of alloy theory. Knowledge of the fundamentals of transformation, diffusion, precipitation and similar areas is essential for the development of new metallic materials.

III. Chemistry of Solids

(a) Order-Disorder Analysis
Dr. Z. W. Salsburg, Department of Chemistry

The Monte Carlo method of estimating statistical mechanical averages in the petit canonical ensemble, described by Rosenbluth et al, Wood and Parker (for fluid systems), and Salsburg et al)for lattice models), has been extended to a general multicomponent lattice model in a restricted grand canonical ensemble. The procedure has been applied to the two-dimensional triangular lattice-gas with periodic boundary conditions at a super-critical temperature ($\beta\epsilon = \ln 2$) and numerical results have been obtained for the energy, specific heat, density, isothermal compressibility, thermal expansion coefficient, and grand partition function (pressure) at $\Delta = 0.1, 0.0, -0.1, -0.2, -0.3, -0.4, -0.6, -0.8$ (with $B = 100$); at $B = 16, 25, 36, 49, 64, 100, 196$ (with $\Delta = 0.0$); where $\Delta = \beta\mu - 3\beta\epsilon$, ϵ is the nearest-neighbor interaction energy, $\beta = (kT)^{-1}$, μ is the chemical potential and B is the number of sites. In order to emphasize the B dependence of Monte Carlo calculations an extensive comparison of the grand canonical and petit canonical calculations were carried out. Properties in both ensembles display the type of irregular B-dependence predicted by Lebowitz and Percus for very small systems. For the larger lattices, properties in the petit ensemble show a stronger B-dependence than in the grand ensemble which is in quantitative agreement with the leading term in the asymptotic analysis. A comparison with the exact analytical results ($B = \infty$, $\Delta = 0$) indicates that the accuracy of the Monte Carlo procedure for the grand ensemble can be reliably estimated by statistical analysis of partial averages over the Markov Chain.

Extensive calculations were also performed to obtain the supercritical thermodynamic properties of a 100-site triangular lattice-gas. Results

were obtained for T_r = 1.15, 1.20, 1.25, 1.30, and 1.40 with Δ = 0.0000, -0.0400, -0.2000, and -0.4000 on each isotherm. These results are compared with those obtained from two analytical approximations and with the exact results for the infinite lattice.

We now have an adequate numerical procedure for obtaining order-disorder properties of binary systems (including metallic alloys) for all temperatures and pressures except in the two-phase region. Our study has made it clear that there is still room for improvement in Monte Carlo procedures and such advances must be made before the two-phase region can be analyzed.

(b) Kinetic Measurements of the Rate of Oxidation of Nickel Foils at Elevated Temperatures
Dr. W. W. Akers, Department of Chemical Engineering

During the past six months the temperature measurement technique, involving Kelvin bridge type resistance measurements, has been further refined and has been employed with the nickel foils in oxygen at 760 mm Hg. Reproducibility has been obtained within the order of accuracy of the measurements (± 5%). Weight determination measurements have been resumed and although smooth curves of oxidation extent are obtained, the reproducibility is not yet satisfactory and these determinations are continuing.

The spot welding of lead wires to the foils which has been the critical step and a bottleneck in the temperature measurement procedure has been facilitated by the availability of a Weldmatic spotwelder. Temperature curves have been obtained with two settings on the flash capacitor bank. On the lower one, the clean bare foils reached a peak temperature of 700°C. After a certain amount of oxidation (about 20 flash heating periods) the peak temperature leveled at 1100°C. At the higher setting the peak temperature rose from 880°C on the bare metal to 1430°C with oxidized foil, reaching the latter value after 8 flash heating periods. Use of two lengths of foil again verified the assumption that the cooling effects on the lead wires is negligible for the first 100 milliseconds

The difficulty in reproducing the oxidation determination is mainly due to difficulty in orienting the foils suspended by the quarts fiber springs. A small magnet outside of the flash chamber is now being used to control this orientation. In addition, a more careful calibration of the voltmeter measuring the capacitor voltage is now being employed to assure reproducibility of the flash intensity. It is expected that these changes will considerably improve the reproducibility of the oxidation determinations.

(c) Measurement of Emissivity of Nickel and Nickel-Oxide Surfaces at Elevated Temperatures
Dr. W. W. Akers, Department of Chemical Engineering

Mechanical, chemical and electrochemical methods of polishing nickel wires were studied. The mechanical method was discarded because it could not be used for long sections of fine wires. Chemical polishing was also discarded because severe pitting could not be eliminated. Electrochemical experiments

were made to determine the effect of current density, solution temperature and composition, electrode geometry, and degree of agitation of the solution upon the polishing action. In determining the degree of polishing, we considered these surface imperfections; pits, undulations, etch marks, and small peaks. Conditions were found that produced a satisfactory polish.

Equipment was made to determine the resistance of wire samples between ambient and 800°C in controlled atmospheres between atmospheric pressure and 10^{-6} torrs. A minimum precision of 0.1% is obtained in the resistance of 0.01 ohm samples. The drift of resistance was studied when samples were subjected to heat cycles in oxygen, hydrogen, and vacuum. An initial annealing step proved effective in reducing subsequent drift to a small value.

Special instrumentation equipment was assembled to eliminate parasitic dc emf's in measuring circuits. Contact matching and thermostating techniques were utilized to achieve a dc noise level of less than 1 microvolt.

A numerical study was begun to investigate the temperature distribution in electrically heated wires. The heat transfer equation is nonlinear and is peculiarly affected by the changes in properties of nickel and its Curie point.

(d) Mass-Spectrometric Studies of High Temperature Interactions between Gases and Condensed Phases
Dr. J. L. Margrave, Department of Chemistry

Personnel to work on this project arrived in Houston during February 1963. The new laboratories became available for occupancy on April 8, 1963, and considerable headway has been made in ordering and designing of equipment and in plans for experiments to be done using the Bendix mass spectrometer (delivered May 13, 1963) alone and in combination with the rotating disc velocity selector. It is expected that preliminary test runs with the Bendix mass spectrometer will be completed in May and, therefore, that significant experiments concerning gas-solid interactions of various sorts (Langmuir and Knudsen experiments, reflection and evaporation coefficient studies, and studies of monoenergetic atomic beams) should be underway this summer.

Studies of gas-condensed phase interactions at high temperatures provide data for evaluation of new materials under the extreme types of conditions to which space vehicles may be exposed, e.g., high temperatures, low pressures, oxidizing atmospheres, etc.

(e) Investigation of Some Thermodynamic Properties of Inorganic Halides at High Temperatures
Dr. T. E. Brackett, Department of Chemistry

During the past six months the calorimetric investigation of Al_2O_3 and NaCl was concluded and prepared for publication; the calorimeter was moved and reinstalled elsewhere in the building; and the investigation of $BaCl_2$ initiated.

Also the crystal structure investigations of the Barium Halides was concluded, as was a similar investigation of Calcium Bromide. The structural work on lead chloride and strontium bromide is continuing.

It is hoped that all of these investigations will be concluded by the end of June, 1963.

(f) The Nature of the Hydrogen Bond
Dr. R. L. Sass, Department of Chemistry

During the past six months various models have been tested in an attempt to correlate the known crystal structures of the aliphatic carboxylic acids and the available thermodynamic data. A satisfactory model based on the vibrational states of the terminal methyl group of the fatty acid chain quantitatively explains the variation in melting points and heats of fusion between acids of even numbers of carbon atoms and those of odd numbers of carbon atoms. Further calculations are now in progress to calculate the total crystal energy of these molecules.

A satisfactory trial structure has been obtained for the molecule cyclononatriene.

(g) Crystal Structures of Alkaline Earth Halides
Dr. R. L. Sass, Department of Chemistry

The structures of barium chloride, bromide and iodide have been refined from powder X-ray diffraction data as well as that of calcium bromide. The reported structure of strontium bromide has been found to be that of the monohydrate. Work on anhydrous strontium bromide shows it to crystallize with a tetragonal symmetry different from that observed for any other salt of the type AB_2. The final structure of this compound has not as yet been obtained and attempts to grow single crystals have thus far been unsuccessful.

(h) Radiation Effects on Metallic Films and Surfaces of Solids
Dr. T. W. Leland, Department of Chemical Engineering

A new series of experiments has been undertaken to extend the initial studies of radiation effects on MgO published in J. Phys.Chem. 66, 2591 (1962). The new investigations are to study the role of H_2O adsorbed on the surface in influencing the radiation effects on the catalytic activity of MgO. An apparatus has just been completed to dose MgO samples with measured quantities of adsorbed water.

A series of studies has been completed on the effect of H_2 adsorption on the electrical condictivity and Seebeck EMF of CdS^{35} radioactive films. The important conclusions are:

(i) The chief effects are due to the chlorine daughter impurities rather than the β radiation.

(ii) The rate of ionized adsorption of H_2 on radioactive CdS^{35} films decreases as the S^{35} decay continues.

(iii) The decrease in adsorption rate has been related to the increase in Fermi level in the solid produced by the chlorine impurities built up by the decay.

(i) Chemisorption on Solid Supports
Drs. H. A. Deans and T. W. Leland, Department of Chemical Engineering

The study of chemisorption on various solid supports, employing new pertubation chromatographic techniques, is continuing. Apparatus is under construction to encompass a wide range of surface coverages and temperatures. A new large volume temperature bath capable of high temperatures has been constructed and tests on the bath and on the system equipment are being carried out at high temperatures. A new detector apparatus able to measure very small perturbations in composition is under construction.

(j) Study of Hydrates
Dr. R. Kobayashi, Department of Chemical Engineering

(i) Experimental Program

The experimental technique developed to study hydrate formation conditions for binary gas-water systems has been utilized to study the nitrogen-water system and developed to study the mixed hydrates of methane-argon-water system. The studies of nitrogen were carried out to 50,000 lbs. per sq. in. and the studies of the methane-argon-water system to pressures as high as 17,000 lbs. per sq. in. The data confirms the applicability of the method based on the observation of a finite break in the pressure-temperature locus for a constant volume system at the three-phase hydrate-liquid-gas locus to a ternary system.

(ii) The statistical mechanical solid solution theory of Platteeuw and van der Waals has been extended above the ice point and applied to predict the experimentally determined gas-liquid-hydrate equilibrium loci for methane, argon, and nitrogen up to a pressure of 50,000 psia.

The agreement of the theory and experiment was excellent for methane-water and the argon-water system, but showed a slight discrepancy for the nitrogen-water system. Apparently, the deviation of the nitrogen molecules from the spherical model assumed in the theoretical model is sufficient to introduce the discrepancies.

(iii) Theoretical Prediction of Hydrate Formation Conditions for Ternary Systems: The Methane-Argon-Water Systems

The solid solution theory of Platteeuw and van der Waals has been extended and applied to the three component, methane-argon-water system above 32°F over the range of the experimental studies outlined in (i). Good agreement of theory with experiment was again found to hold.

29 May 1963

Franz R. Brotzen

Dean of Engineering

Appendix to Status Report #8

Papers Published and Manuscripts Submitted

In the Period

Beginning November 1, 1962 and Ending April 30, 1963

R. Dawson, E. B. Brackett, and T. E. Brackett
"A High Temperature Calorimeter; the Enthalpies of α-Aluminum Oxide and Sodium Chloride"
Submitted for publication to Jnl. Phys. Chem.

D. F. Marshall and R. Kobayashi
"Hydrates at High Pressures: Methane-Water and Argon-Water Systems"
Submitted for publication to Am. Inst. of Chem. Engrg. Jnl.

J. H. Lunsford and T. W. Leland, Jr.
"Effects of Neutron and Ultraviolet Irradiation on the Catalytic Activity of Magnesium Oxide"
Published in Jnl. Phys. Chem., vol. 66, 2591 (1962)

S. Okuda
"Internal Friction Peaks in Silver and Platinum at Low Temperatures"
Published in Appl. Phys. Ltrs., vol. 2, 163 (1963)

D. E. Hartman and J. M. Roberts
"The Temperature Dependence of the Microyield Points in Prestrained Magnesium Single Crystals"
Submitted for publication to Acta Met.

S. Okuda
"Low Temperature Internal Friction in Gold and Copper"
Submitted for publication to Jnl. Appl. Phys.

F. J. Streiter, D. H. Templeton, F. Scheuerman and R. L. Sass
"The Crystal Structure of Propionic Acid"
Published in Acta Cryst., vol. 15, 1233 (1962)

D. A. Chesnut
"Monte Carlo Calculations for the Two-Dimensional Triangular Lattice Gas, Super-critical Region"
Submitted for publication to Jnl. Chem. Phys.

R. M. Asimow
"Quenched-in Resistivity in Dilute Alloys"
Submitted for publication to Acta Met.

E. B. Brackett, T. E. Brackett and R. L. Sass
"The Crystals Structure of Calcium Bromide"
Submitted for publication to Jnl. Inorg. and Nucl. Chem.

S. Okuda
"Study of the Bordoni Peak in FCC Metals after Deformation at 4.2°K and Subsequent Low-Temperature Annealing"
Published in Jnl. Phys. Soc. Japan, vol. 18, Suppl. 1, 187 (1963)

J. M. Roberts and D. E. Hartman
"Theory of Dislocation Hysteresis with Application to Damping Measurements in Magnesium Single Crystals"
Published in Jnl. Phys. Soc. Japan, vol. 18, Suppl. 1, 119 (1963)

T. E. Brackett, E. B. Brackett and R. L. Sass
"The Crystal Structures of Barium Chloride, Bromide and Iodide"
Submitted for publication to Jnl. Phys. Chem.

D. A. Chesnut and Z. W. Salsburg
"A Monte Carlo Procedure for Statistical Mechanical Calculations in a Grand Canonical Ensemble of Lattice Systems"
Submitted for publication to Jnl. Chem. Phys.

D. M. Barnett and J. M. Roberts
"A Discussion of the Importance of Line Tension on Cottrell's Theory of the Sharp Yield Point"
Submitted for publication to Trans. Am. Inst. Min., Met. and Petr. Engrs.

J. M. Roberts and N. Brown
"Nonelastic Strain Recovery in Zinc Single Crystals"
Published in Acta Met., Vol. II, 1, 7 (1963)

R. M. Asimow
"Clustering Kinetics in Binary Alloys"
Published in Acta Met., Vol. II, 72 (1963)